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(54) **Nanotubes of crystalline titania and process for producing the same**

Kristalline Titanoxid-Nanoröhrchen und Verfahren zu ihrer Herstellung

Nanotubes d'oxyde de titane cristallin et procécé pour leur préparation

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- **P. HOYER: "FORMATION OF TITANIUM DIOXIDE NANOTUBE ARRAY" LANGMUIR, vol. 12, 1996, pages 1411-1413, XP002052967**
- **LAKSHMI B B ET AL: "SOL-GEL TEMPLATE SYNTHESIS OF SEMICONDUCTOR NANOSTRUCTURES" CHEMISTRY OF MATERIALS, vol. 9, no. 3, March 1997, pages 857-862, XP000686528**
- **KASUGA: "IMPROVEMENT OF PHOTOCATALYTIC ACTIVITY OF TIO2-BASED POWDERS PREPARED BY A SOL-GEL METHOD" PREPRINTS OF ANNUAL MEETING OF THE CERAMIC SOCIETY OF JAPAN, XP002052939**

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Description

[0001] Titania (TiO_2) has excellent ultraviolet absorbability, absorbent properties and the like. Accordingly, it has been widely used as

1) an ultraviolet absorber, as a masking agent in anti-sunburn agents, in paints, in films and the like; and

2) as an absorber, an adsorbent, a deodorizer and the like.

[0002] Furthermore, the superior photocatalytic activity of titania is of interest. The titania is applied to environmental cleanup or the like, for the decomposition of carbonaceous gas or nitrogen oxides whilst utilizing its superior oxidation and reduction properties.

[0003] The improvement of the properties of titania, especially the photocatalytic activity in the above-mentioned usages has been in demand.

[0004] One of the conventional technologies for improving the properties of titania is by doping with SiO_2, producing an increased specific surface area.

[0005] In order to improve the photocatalytic activity, the present inventors tried to chemically treat TiO_2 powder obtained by a sol-gel method and having a large specific surface area with an NaOH aqueous solution to improve the photocatalytic activity, and reported this technology in the following literature:

(1) "Preprints of Symposium of Catalyst Chemistry related to Light", June 6 1996, held by Rikagaku Kenkysusyo and Catalyst Academy, p. 24 - 25;

(2) "Preprints of Annual Meeting of The Ceramic Society of Japan 1996", April 2 to 4, 1996, p. 170.

[0006] Aiming at improving the catalytic activity as the properties of crystalline titania, further investigations were made. They found that where the crystalline titania is treated with an alkali, if certain conditions are met, a titania crystal in a nanotube form which has hitherto been unknown is formed, leading to the accomplishment of the present invention.

[0007] Nanotubes of anastase titania having an outer diameter of between 140 and 180 nm are disclosed in P. Hoyer's "Formation of titanium dioxide nanotube array", Langmuir, vol. 12, 1996 p. 1411-1413. The document also discusses an electrodeposition process for producing the nanotubes which involves the addition of $NaHCO_3$ to the electrolyte solution

[0008] The present invention is to provide crystalline titania in a nanotube which is a novel crystal shape. The diameter of the nanotube varies depending on the production conditions and the like. It is approximately between 5 and 80 nm in many cases. The crystal structure which is easy to obtain is an anatase type.

[0009] This nanotube is formed by treating crystalline titania with an alkali. In order to increase the yield, the alkali treatment can be conducted at a temperature of from 18 to 160°C using from 13 to 65 percent by weight of sodium hydroxide expressed as parts of sodium hydroxide per 100 parts of solvent (water).

[0010] Since the nanotube is a hollow crystal, the specific surface area is increased as compared with a solid crystal such as a needle crystal, and the specific surface area in the volume occupied is increased. Accordingly, it is expected to markedly improve the properties of the crystalline titania. Furthermore the crystal is expected to find novel use in filters and the like by utilizing the nanotube shape.

Brief Description of the Drawings

[0011] Fig.1 is a view showing a model shape of crystalline titania in the present invention.

[0012] Fig.2 is a transmission electron micrograph of Sample No.1-11 (40% x 110°C x 20 hours) in the Examples.

Description of the Preferred Embodiments

[0013] The crystalline titania of the present invention is a nanotube as shown in Fig.1

[0014] The diameter of this nanotube varies depending on the production conditions. It is usually between approximately 5 and 80 nm. The length thereof also varies depending on the production conditions. It is usually between 50 and 150 nm. The thickness thereof is usually between 2 and 10 nm.

[0015] With respect to the crystal system of this nanotube, the anatase type is easily obtainable as shown in Tables 1 and 2.

[0016] The process for producing crystalline titania in the present invention is described below. In the following description, "% by weight" which refers to the alkali concentration means parts of alkali per 100 parts of solvent (water).

[0017] The crystalline titania which has a nanotube shape in the present invention is produced by treating a titania powder with an alkali.

(1) Production of a titania powder.

[0018] The titania powder (crystalline titania) used herein has a particle diameter of, usually from 2 to 100 nm, preferably from 2 to 20 nm whether it is an anatase type or a rutile type.
[0019] Examples thereof include titania powders produced from a titanium ore such as anatase, rutile, brookite and the like by the following known liquid phase method, vapor deposition method or sol-gel method.
[0020] "Vapor deposition method" here referred to is a method in which titania is produced by hydrolysing a titanium ore by heating a strong acid such as sulfuric acid or the like, and heating the resulting hydrous titanium oxide at from 800 to 850°C.
[0021] "Liquid phase method" here referred to is a method in which titania is produced by contacting TiCl, with O_2. and H_2.
[0022] "Sol-gel method" here referred to is a method in which titania is produced by hydrolysing titanium alkoxide including $Ti(OR)_4$, in an alcohol aqueous solution to form a sol, adding a hydrolase to the sol, allowing the mixture to stand for gelation, and heating the gel.

(2) Alkali Treatment

[0023] In the alkali treatment, a titania powder is dipped in from 13 to 65% by weight of sodium hydroxide at a temperature of from 18 to 160°C for from 1 to 50 hours. Preferably, it is dipped in from 18 to 55% by weight of sodium hydroxide at a temperature of from 18 to 120°C. More preferably, it is dipped in from 30 to 50% by weight of sodium hydroxide at a temperature of from 50 to 120°C for from 2 to 20 hours. At this time, when the alkali concentration is high, the temperature may be low (refer to Sample Nos. 1-9 and 2-4). When the temperature is high, the alkali concentration may be relatively low (refer to Sample Nos.1-8 and 2-3).
[0024] When the concentration of sodium hydroxide is less than 13% by weight, the reaction time may be too long to form a tube, and it is not efficient from the industrial viewpoint. When it exceeds 65% by weight, the tube is hardly formed (refer to Sample Nos.1-15, 1-16, 1-17, 2-10, 2-11 and 2-12). When the temperature is less than 18°C, the reaction time for forming a tube is prolonged. When the temperature exceeds 180°C, the tube is hardly formed.
[0025] As supported in Examples to be described later, the nanotube crystal aggregate can hardly be produced without the above-mentioned ranges. Alkali treatment may be conducted in an open vessel, that is, under normal pressure (at atmospheric pressure). It is, however, advisable to conduct it in a sealed vessel. The evaporation of water is suppressed in the sealed vessel to stabilize the alkali concentration. When the temperature is increased to 100°C or more in the sealed vessel, the pressure is increased and a nanotube having a small diameter is easily produced as compared with the alkali treatment in an open vessel. When the alkali treatment is conducted in the sealed vessel under increased pressure of 1.5 atm (calculated), a nanotube having a small diameter of from 5 to 10 is obtained.
[0026] The alkali treatment includes a step of water-washing as a final step. It is advisable to neutralise the resulting product with an inorganic acid such as dilute hydrochloric acid or the like.

(3) Heat Treatment.

[0027] The above-obtained nanotube titania may further be heat-treated at from 200 to 1,200°C for from 10 to 400 minutes, preferably at from 300 to 800° for from 60 to 160 minutes. This heat treatment is expected to improve the crystallinity of TiO_2 and to increase the catalytic activity. The nanotube does not collapse through this heat treatment. Further, it does not collapse either upon using a pulverizer.

(4) Use

[0028] The specific surface area of the above-obtained nanotube titania in the present invention is by far larger than that of the spherical or needle crystal.
[0029] Consequently, when this titania is used as an ultraviolet absorber, a masking agent, an adsorbent or an optically active catalyst, the increase in the specific surface area can be expected, and especially the specific surface area per unit volume can be greatly improved.
[0030] When this titania is used as a catalyst, it may be ordinarily supported on a metal such as platinum, nickel, silver or the like.
[0031] This nanotube titania can be used in such as (a) a filter; (b) a material with a new performance which is obtained by inserting an organic, inorganic, or metal material therein; and (c) a magnetic substance with new magnetic

properties which is obtained by inserting a magnetic material therein.

[0032] The present invention is illustrated by way of Example.

(1) Production of starting crystalline titania:

[0033] In order to give a composition of the formula

$$xTiO_2 . (1\text{-}x)SiO_2$$

wherein x is 1 or 0.8,
commercial tetraisobutoxytitanium and tetraethoxysilane were dissolved in an ethanol solution to conduct hydrolysis. To the resulting sol was added dilute hydrochloric acid as a hydrolase, and the mixture was allowed to stand for gelation.

[0034] The gel was heated with an electric oven at 600°C for 2 hours. Then, the heated product was pulverised using an agate mortar to obtain a fine powder.

[0035] The following two types of starting crystal titania, 1) and 2), were prepared by this sol-gel method.

i) TiO_2 ... average particle diameter; approximately 15 nm, specific surface area: 50 m^2/g

ii) $0.8TiO_2 . 0.2SiO_2$ ... average particle diameter; approximately 6 nm, specific surface area: 10 m^2/g

Additionally, the following commercial crystal titania A was used as a starting crystal.

iii) Commercial crystal titania A

Anatase-type crystal titania (TiO_2) produced by reacting an ilemnite ore with sulfuric acid by a vapor deposition method:

average particle diameter: approximately 20 nm specific surface area: 50 m^2/g

(2) Conditions of Alkali Treatment

[0036] Each of the titania powders was treated with alkali under conditions shown in Tables 1 and 2 (those other than Sample No.1-12 and 2-7 were treated in a sealed vessel). The treated powders were subsequently neutralized with 0.1N-HCl aqueous solution. In this manner, the test powders were prepared.

[0037] Each of the test powders was dispersed in an ethanol aqueous solution. A droplet of the dispersion was dropped on a test stand using a pipet, and observed using a transmission electron microscope to estimate the shape of the crystalline titania.

[0038] The results are shown in Tables 1 and 2. From the results in these tables, it is understood that no nanotube crystalline titania is obtained when the alkali concentration is too low or too high.

[0039] In Tables 1 and 2, each judgements mean as follows:

"x" : A Comparative Example not within scope of the present invention.

"Δ" : An Example which produces a nanotube partially

"○" and "◎" : An Example which produces a nanotube excellently. The judgements of "○" or "◎" depend on a specific surface area of each sample. The judgements of them are not always proper when a product requires other properties.

[0040] In Tables 1 and 2, the terms have the following meanings

"%" : percent by weight
"tube/particle" : Particles are incorporated in tubes.
"particle/tube" : Tubes are incorporated in particles.

[0041] In the crystalline titania in Table 1, x in the SiO_2 component was reduced to approximately 0.01 through the alkali treatment. As shown in Table 2, even when the starting crystalline titania was composed of 100% TiO_2, the nanotube titania crystal was obtained. It is thus clarified that the precipitation of titania nanotube has nothing to do with the addition of SiO_2.

Table 1

Composition: $0.8TiO_2 \cdot 0.2SiO_2$					
Sample No.	Conditions of alkali treatment	Type and shape of crystal precipitated		Specific surface area (m^2/g)	Judgement
1-1	2.5% × 100 °C × 60h	anatase	particle	230	×
1-2	5.0% × 100 °C × 60h	↑	↑	230	×
1-3	10% × 100 °C × 20h	↑	↑	230	×
1-4	15% × 60 °C × 20h	↑	tube/particle	250	Δ
1-5	15% × 150 °C × 5h	↑	↑	250	Δ
1-6	20% × 20 °C × 20h	↑	↑	250	Δ
1-7	20% × 60 °C × 20h	↑	↑	250	Δ
1-8	20% × 110 °C × 20h	↑	tube	300	○
1-9	40% × 20 °C × 20h	↑	↑	320	○
1-10	40% × 60 °C × 20h	↑	↑	340	◎
1-11	40% × 110 °C × 20h	↑	↑	420	◎
1-12	40% × 110 °C × 10h (reflux)	↑	↑	480	◎
1-13	60% × 60 °C × 20h	↑	particle/tube	400	Δ
1-14	60% × 60 °C × 40h	↑	↑	400	Δ
1-15	68% × 60 °C × 2h	-	particle	320	×
1-16	68% × 60 °C × 30h	-	↑	350	×
1-17	68% × 110 °C × 20h	-	↑	400	×

× : Comparative Example (no good)
Δ : Example (fair)
○ : Example (good)
◎ : Example (excellent)

Table 2
Composition: TiO_2

Sample No.	Conditions of alkali treatment	Type and shape of crystal precipitated		Specific surface area (m^2/g)	Judgement
2-1	20% × 20 ℃ × 20h	anatase	tube/ particle	200	△
2-2	20% × 60 ℃ × 20h	↑	↑	200	△
2-3	20% × 110 ℃ × 20h	↑	tube	300	○
2-4	40% × 20 ℃ × 20h	↑	↑	200	○
2-5	40% × 60 ℃ × 2h	↑	↑	400	◎
2-6	40% × 110 ℃ × 20h	↑	↑	420	◎
2-7	40% × 110 ℃ × 20h (reflux)	↑	↑	500	◎
2-8	60% × 60 ℃ × 20h	↑	particle/ tube	400	△
2-9	60% × 60 ℃ × 40h	↑	↑	400	△
2-10	68% × 60 ℃ × 10h	—	particle	300	×
2-11	68% × 60 ℃ × 20h	—	↑	350	×
2-12	68% × 110 ℃ × 20h	—	↑	400	×
2-13	40% × 110 ℃ × 20h ※	anatase	tube	300	○

※ : Commercial product A
× : Comparative Example (no good)
△ : Example (fair)
○ : Example (good)
◎ : Example (excellent)

Claims

1. A crystalline titania **characterised in that** the crystal shape is a nanotube having diameter between 5 and 80 nm.

2. The crystalline titania of claim 1, wherein the crystal structure is an anatase type.

3. A process of producing crystalline titania of which the crystal shape is a nanotube, which comprises treating crystalline titania with NaOH.

4. The process of claim 3, wherein the nanotube has approximately an outer diameter between 5 and 80 nm.

5. The process of claim 3, wherein the NaOH treatment is conducted at a temperature of from 18 to 160°C using from 13 to 65 percent by weight of sodium hydroxide.

6. The process of claim 3, wherein said NaOH treatment is conducted at a temperature of from 18 to 120°C using from 18 to 55 percent by weight of sodium hydroxide.

7. The process of claim 6, wherein said NaOH treatment is conducted at a temperature of from 50 to 120°C using from 30 to 50 percent by weight of sodium hydroxide.

8. The process of claim 3, wherein said NaOH treatment is conducted under increased pressure in a sealed vessel.

9. The process of claim 3, wherein after treating the crystalline titania with NaOH, the product is washed with water and then neutralised.

10. The process of claim 3, wherein after said NaOH treatment, the product is further heat-treated at a temperature of from 200 to 1,200°C for from 10 to 400 minutes.

Patentansprüche

1. Kristallines Titandioxid, **dadurch gekennzeichnet, dass** die Kristallform ein Nanoröhrchen mit einem Durchmesser zwischen 5 und 80 nm ist.

2. Kristallines Titandioxid nach Anspruch 1, worin die Kristallstruktur ein Anatas-Typ ist.

3. Verfahren zur Herstellung von kristallinem Titandioxid, dessen Kristallform ein Nanoröhrchen ist, das umfasst das Behandeln von kristallinem Titandioxid mit NaOH.

4. Verfahren nach Anspruch 3, worin das Nanoröhrchen etwa einen äußeren Durchmesser zwischen 5 und 80 nm aufweist.

5. Verfahren nach Anspruch 3, worin die NaOH-Behandlung bei einer Temperatur von 18 bis 160°C unter Verwendung von 13 bis 65 Gew.-% Natriumhydroxid durchgeführt wird.

6. Verfahren nach Anspruch 3, worin die genannte NaOH-Behandlung bei einer Temperatur von 18 bis 120°C unter Verwendung von 18 bis 55 Gew.-% Natriumhydroxid durchgeführt wird.

7. Verfahren nach Anspruch 6, worin die genannte NaOH-Behandlung bei einer Temperatur von 50 bis 120°C unter Verwendung von 30 bis 50 Gew.-% Natriumhydroxid durchgeführt wird.

8. Verfahren nach Anspruch 3, worin die genannte NaOH-Behandlung unter erhöhtem Druck in einem versiegelten Behälter durchgeführt wird.

9. Verfahren nach Anspruch 3, worin nach der Behandlung des kristallinen Titandioxids mit NaOH das Produkt mit Wasser gewaschen und dann neutralisiert wird.

10. Verfahren nach Anspruch 3, worin das Produkt nach der Behandlung mit NaOH 10 bis 400 min lang einer weiteren Wärmebehandlung bei einer Temperatur von 200 bis 1200°C unterworfen wird.

Revendications

1. Titane cristallin **caractérisé en ce que** le cristal est en forme de nanotube présentant un diamètre situé entre 5 et 80 mm.

2. Titane cristallin selon la revendication 1, **caractérisé en ce que** la structure cristalline est de type anatase.

3. Procédé de fabrication de titane cristallin dont le cristal est en forme de nanotube, **caractérisé en ce qu'**il comprend une étape de traitement du titane cristallin par NaOH.

4. Procédé de fabrication selon la revendication 3, **caractérisé en ce que** le nanotube présente un diamètre sensiblement compris entre 5 et 80 mm.

5. Procédé de fabrication selon la revendication 3, **caractérisé en ce que** le traitement par NaOH est effectué à une

température située entre 18 et 160°C en utilisant de 13 à 65 pourcents en poids d'hydroxyde de sodium.

6. Procédé de fabrication selon la revendication 3, **caractérisé en ce que** le traitement par NaOH est effectué à une température située entre 18 et 120°C en utilisant de 18 à 55 pourcents en poids d'hydroxyde de sodium.

7. Procédé de fabrication selon la revendication 6, **caractérisé en ce que** le traitement par NaOH est effectué à une température située entre 50 et 120°C en utilisant de 30 à 50 pourcents en poids d'hydroxyde de sodium.

8. Procédé de fabrication selon la revendication 3, **caractérisé en ce que** le traitement par NaOH est effectué sous forte pression dans un récipient étanche.

9. Procédé de fabrication selon la revendication 3, **caractérisé en ce qu'**après le traitement du titane cristallin avec NaOH, le produit est lavé à l'eau puis neutralisé.

10. Procédé de fabrication selon la revendication 3, **caractérisé en ce qu'**après le traitement par NaOH, le produit est en outre traité par la chaleur à une température allant de 200 à 1.200°C pendant de 10 à 400 minutes.

Fig. 1

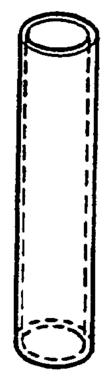

Fig. 2